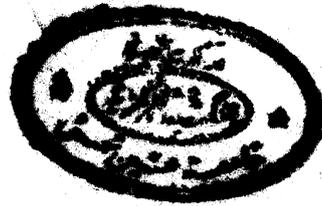


THE S I S
ON
CERTAIN ADSORPTION CHARACTERISTICS OF
SOME EGYPTIAN DIATOMACEOUS EARTHS

Presented to
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THE PLAIN CONCEPT OF ORGANIC CHEMISTRY OF
SOME APPLIED DIATOMACEOUS LAMINAE

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N O T E

Besides the work presented in this thesis the candidate attended post graduate courses for two years in Advanced Surface, Inorganic, and Electro Chemistry and he has successfully passed an examination in these topics.

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(1) INTRODUCTION.

Diatomaceous earth, which is known under numerous designations such as diatomite, German kieselguhr and tripolite⁽¹⁾, etc. consists of the siliceous, friable and porous remains of microscopic aquatic organisms known as diatoms. The pores of diatomite are partially or completely filled with silica.⁽²⁾ The diatoms are present in different forms: elongated, filiform, spicular or acicular. Materials composed of individuals of the acicular form, the length of which varies from 0.093 to 0.156 mm and the thickness of which varies from 0.00156 - 0.00468 mm, are the best suited for technical purposes.

Diatomaceous earth varies in colour from white, grey, yellowish, brownish to greenish. It is very light, floating on water. Specific gravity of air dried material is 0.24 and of the calcined material 0.34.

Tripolite differs from diatomite in being more compact with laminated structure and consequently denser (sp.gr.1.86) and less porous. It merely represents the same material of older geologic age.⁽³⁾

Diatomite occurs and is mined in many countries in Europe, e.g. Germany, Italy, Czechoslovakia, U.S.S.R. The world's largest and purest deposits are probably those occurring in the United States.⁽¹⁾ The purest form of diatomaceous earth is composed chiefly of opaline silica but in most commercial deposits the material contains impurities.

Chemically it consists of hydrated silica, mixed with various impurities, such as sand, hydroxides of iron, clay or calcareous substances or organic matter. The silica content varies approximately between 70 and 90%. The following are some analysis results of diatomaceous earth from some districts :

Diatomite is marketed in three general types; natural, calcined and flux-calcined. The natural product is dried, ground and if necessary air classified. The calcined product is heated to a fairly high temperature to remove moisture and organic matter, and air classified. The flux calcined or "White" product is obtained and calcined in rotary kilns (at temperatures up to 1204°C).

Table 1. Analysis of some diatomaceous earths

	Aurillac	Armenia U.S.S.R. (4)	Scotland U.K.	Virginia U.S.A.
SiO ₂	91.61	67.1	88.73	75.86
TiO ₂	0.10	0.23	- -	- -
Al ₂ O ₃	1.53	7.36	- -	9.88
Fe ₂ O ₃	2.22	3.9	0.67	2.92
CaO	0.18	5.1	0.04	0.29
MnO	- -	0.31	- -	- -
MgO	0.29	1.51	- -	1.73
K ₂ O	Trace	1.80	- -	
Na ₂ O	Trace		- -	
H ₂ O	2.33	6.1	6.4	8.37
Org.Matter	1.74	7.14	4.15	- -

Uses of Diatomaceous Earth :

Diatomite finds unlimited applications and uses since earlier times. The following are examples of its uses:

- (1) It is used as a filler for the manufacture of light weight chemicals. (9)
- (2) It is added to concrete and mortar, (6-7) and in the manufacture of light brick stones for insulating purposes.
- (3) It is used as a filler (8-12) in the manufacture of rubber, plastics and paper.
- (4) It can be used as a filter aid (13-17), as in sugars, wine, brewery, and acids production. According to Cummins (18) the fundamental function of a filter aid is to provide a porous cake structure. The particle size, specific surface, cake porosity, etc.. affect the choice and use of a filter aid. The following table shows the general characteristics of 6 diatomaceous filter aids:

Table II General Characteristics of Diatomaceous Filter Aids (18)

	Condition	App. density lb/cu.ft.	General Particle size dis-tribution microns	Approx. surface area sq./g.
Filter cel	natural	8.5	1-12	30,000
Stand.Super-cel	Calcined	9.2	Mostly 2-11	20,000
Hyllo-Super-cel	Flux-calcined	9.7	Mostly 4-20	10,000
Celite 503	Flux-calcined	10.5	5-30	8,000
Celite 535	Flux-calcined	11.0	18-38	7,000
Celite 545	Flux-calcined	11.5	12-45	6,000

The filtration rate of the liquid to be filtered increased from filter cel (particle size 7-12 microns, specific surface 30,000 cm²/g) to celite 545 (particle size 12-45 microns, specific surface 6,000 cm²/g) whereas the clarity showed the inverse relationship being definitely best for filter cel and poorest for celite 545. The cake porosity was determined by particle size as well as particle shape. It can be noticed that as the particle size increases the apparent density increases while the specific surface area decreases.

(5) Owing to its high adsorption power it is added as a discolouring agent in oil and grease production. According to Kress and Trucano⁽¹⁹⁾ diatomaceous earth have or silicas an affinity for basic dyes but not for acid dyes; amorphous silicas have a greater adsorptive power than the crystalline types.

Tsuchiya⁽²⁰⁾ studied the decolourising power of diatomaceous earth by using methylene blue solution containing 0.5, 1.0 and 1.5 g/l. Teletov⁽²¹⁾ and Teletov et al⁽²²⁾ measured the adsorption of benzene and methylene blue on diatomaceous earth of the Kharakov region and they found that the

capillary action depends upon the mineral composition and grain size. In these adsorbents the amorphous silica, calcite shells of diatomaceae and limonite were more adsorbing than other minerals present as quartz and clay minerals. All these components showed a different polarity i.e. charge on the surface, which explained why rocks of Kharakov formation adsorbed such a variety of materials.

- (5) In petroleum⁽²³⁾ industry diatomaceous earth is used as a bearer for sulphuric acid, for absorption of acid sludge and for the separation of water-petrol emulsions, the discolouring of petrol and the cleaning of benzine.
- (7) Diatomaceous earth is also used in the preparation of many explosives and detonates.
- (8) One of the great applications of diatomite is its employment as a basis for catalysis where it acts as a catalyst support⁽²⁴⁻²⁸⁾ or as a catalyst⁽²⁹⁻³²⁾.

Structure of Diatomaceous Earth :

Sakai and Fukami⁽³³⁾ showed by X-ray studies that diatomaceous earth is composed of amorphous silica with

particles so small that no sharp lines appeared on the photograph. In a trial to investigate the shape and structure of diatomaceous earth (kieselguhr) Oatrasvas⁽³⁴⁾ produced photomicrographs (500 x enlargement) of two types of French kieselguhr: the first one showed essentially discs perforated by different diameters, and the second spheroidal, smooth particles without perforations. The first one consequently had the greater surface area.

Bykov⁽³⁵⁾ used the electron microscope studies on natural sorbents as diatomaceous earth to determine their particle size. On the basis of benzene adsorption studies (where specific surface of skeletons of sorbents were calculated) together with thermal analysis and knowledge of chemical composition, Bykov tried to elucidate the principal mineral forms constituting a given natural sorbent. Continuing his studies Bykov⁽³⁶⁻³⁷⁾ used the adsorption-desorption of C_6H_6 and $COCl_2$ vapours to investigate the porosity of the diatomites of the far east.

Luk'yanovich et al⁽³⁸⁾ tried to study the structure of diatomaceous earth using electronmicroscopic photographs. Kamakin⁽³⁹⁾ used the mercury pressure porosimeter

so that the pore dimensions of the sample are smaller than the pore dimensions obtained by means of the pore-size distribution method with pore size distribution found by desorption methods.

Salisarenko et al⁽⁴⁰⁾ studied the structure of Volga diatomaceous earth (grains and powders) by obtaining the sorption-desorption isotherms of H_2O , and C_6H_6 at $20^\circ C$, all the curves were S-shaped with irreversible hysteresis with water vapour and reversible hysteresis with C_6H_6 vapour. The point of beginning of hysteresis agreed with that calculated by the methods of Kiselev⁽⁴¹⁾ and that of Bykov⁽³⁶⁾. The experimental data obtained for grains were more suitable for studying structure than those obtained for powders. Jiru⁽⁴²⁾ et al determined the surface area and structure of some Czechoslovak siliceous earth by measurement of the physical adsorption of nitrogen, apparent and actual densities.

Zallevskii⁽⁴³⁾ et al used the method of introduction of mercury by pressure to study the characteristics of the porous structure of natural adsorbents in the range of transition pores and macropores. Chernoyansk diatomite showed the presence of large pores (presence of abrupt

slaps in the integral structural curve in the low pressure region), and pores of the transition sizes (absence of introduced mercury at high pressure). Most of the micropores of Chernoyarsk and Zhanka earths have radii between 1600-5300 Å.

Zabelin⁽⁴⁴⁾ found by X-ray diffraction study of the crystal structure of a series of diatomaceous earths and tripolites of the Volga region that they were enriched in amorphous material, β -cristobalite was prevalent but often there was also a distinct approximation to α -cristobalite. Differential thermal analysis of the diatomites did not show any $\alpha \rightleftharpoons \beta$ -cristobalite transition phase, heating to 1050°C did not change this modification but it was inverted into α -cristobalite above 1150°C.

Bykov⁽⁴⁵⁾ investigated the structure of uniform and intermediate porosity tripolites and diatomites by determining the adsorption isotherms of H_2O , MeOH, EtOH, and PrOH at 20°C, all the isotherms showed hysteresis and chemisorption. The Brunauer, Emmett and Teller surface area; S , decreased slowly with increasing molecular weight of alcohol.